



Broad absorbing low-bandgap polythiophene derivatives incorporating separate and content-tunable benzothiadiazole and carbazole moieties for polymer solar cells

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ABSTRACT

Three novel low-bandgap (LGB) conjugated polythiophenes (PThBTD_mCz_n) incorporating separate and content-tunable benzothiadiazole and carbazole moieties have been designed and synthesized for application in bulk heterojunction polymer solar cells (PSCs). The absorption spectral, thermal, electrochemical and photovoltaic properties of the random copolymers were investigated. Broad absorption from a single polymer covering the visible region from 300 to 800 nm was observed, which was ideal for highly efficient harvesting of the solar spectrum. DSC analysis showed that the polymers readily crystallized, indicating highly ordered intermolecular packing, which is beneficial for efficient charge-carrier transport. Electrochemical studies indicate desirable HOMO/LUMO levels that enable a high open-circuit voltage while blending them with fullerene derivatives as electron acceptors. Polymer solar cells using 1:1 or 1:2 wt/wt polymer: PC₆₁BM (methanofullerene [6,6-phenyl C61-butiric acid methyl ester] blends as the photoactive layers were fabricated and characterized. The preliminary investigation on the photovoltaic device of the PThBTD_mCz_n polymers gave similar power conversion efficiency of 1.1–1.2% with V_{oc} of 0.64–0.68 V under simulated solar light AM 1.5 G (100 mW/cm²).

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1. Introduction

Harvesting energy directly from sunlight using photovoltaic cells is recognized worldwide as an important solution to the growing energy crisis and environmental pollution. Polymer solar cells (PSCs) have been attracting considerable attention in recent years due to their unique features of low cost, light weight and potential application in flexible large-area devices [1–3]. To realize high power conversion efficiency, the absorption property of the active

layer in polymer solar cells is of crucial importance. An ideal active layer for a polymer solar cell should have a broad and strong absorption spectrum in the UV, visible and near infrared region to match the sunlight spectrum to a large extend [4]. Recently, low-bandgap (LGB) conjugated polymers have been developed and used in polymer solar cells, and the power conversion efficiencies were accordingly improved due to their absorption often correspond to the maximum photon flux of sunlight spectrum [5]. However, LGB polymers often show better absorption at a long-wavelength range, while other parts of sunlight spectrum are being sacrificed. Obviously, the conjugated polymers with not only low-bandgap but also broad absorption bandwidths are desirable for application in PSCs. Meanwhile, the donor–acceptor systems in the LGB

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polymers cause partial intramolecular charge-transfer (ICT) that enables manipulation of the electronic structure (HOMO/LUMO levels) and is beneficial for charge-separation, however, the transport capabilities are not satisfactory due to the space charge limitation [6]. Hence, the main challenge of LBG polymer solar cell engineering towards high power conversion efficiency is to simultaneously possess strong and broad absorption, efficient exciton-generation, charge-separation and transport.

In our efforts to design new semiconducting polymers for PSC application, we became interested in the construction of LBG polymers incorporating hole-transporting moieties with the aim of enhancing the charge-carrier transporting capability. Leclerc and co-workers reported a series of LBG poly(2,7-carbazole) derivatives [7] for use in polymer solar cells and the highest power conversion efficiency of 4.6% has been achieved [7d]. Recently, we presented a highly crystalline alternative copolymer of indolocarbazole and benzothiadiazole-cored oligothiophenes with a good power conversion efficiency of 3.6% [8]. However, the absorption spectra of the LBG polymers reported by Leclerc and us involve two separate absorption bands with a ‘hole’ between them, which will limit the light absorption and the further improvement of the power conversion efficiency. To broaden the absorption spectrum to cover the whole visible region of the solar spectrum, we developed new random copolymers of dibromonated benzothiadiazole-cored oligothiophene, 5,5'-bisstannyl-2,2'-bithiophene and 2,7-dibromocarbazole (for structures, see Scheme 1). The design was based on the consideration that (i) different chromophores within a single polymer correspond to different absorption wavelength at respective high and low-energy band, thus broad absorption may be realized by dye combinations [9,10]; and (ii) the proportion of the benzothiadiazole acceptors and hole-transporting carbazole moieties can be easily adjusted by random copolymerization, thus providing us an opportunity to fine-tune the relative absorption intensity at high energy band and low-energy band, and the charge-carrier transport property. Actually, Ko et al. have developed a semiconducting copolymers based on coplanar thiophene-phenylene-thiophene derivatives with broad

absorption and high power conversion efficiency using random copolymerization strategy [11]. Herein, we would like to describe the synthesis of the copolymers of thiophenes, benzothiadiazole and carbazole (PThBTD_mCz_n), fundamental UV-vis, thermal and electrochemical properties and their solar cell performance [12].

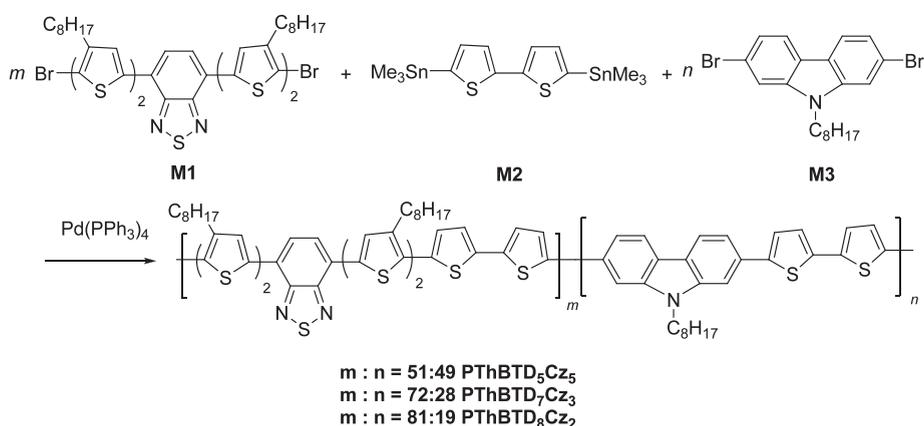
2. Experimental section

2.1. Materials

All reagents and solvents were purchased from JKchemicals and Alfa Chemicals. Anhydrous tetrahydrofuran was distilled over sodium/benzophenone under Ar prior to use.

2.2. Characterization

NMR spectra were recorded on a Varian 500 spectrometer using tetramethylsilane as internal references. Number- and weight-average molecular weights of the polymers were determined by gel permeation chromatography (GPC) on a Waters 410 instrument with polystyrene as standards and THF as eluent. UV-vis spectra were measured using a PerkinElmer Lambda 900 UV-vis-NIR Spectrometer. Thermal properties of the polymers were analyzed with a Perkin-Elmer-TGA 7 instrument under nitrogen at a heating rate of 10 °C min⁻¹. Thermogravimetric analysis (TGA) was carried out using TA instruments TGA Q500 in air. Cyclic voltammetry experiments were carried out on an EG&G Princeton Applied Research potentiostat/galvanostat (model 2273) in an electrolyte solution of 0.1 M tetrabutylammonium perchlorate (Bu₄NClO₄) in acetonitrile. A three-electrode cell was used in all experiments. Platinum wire electrodes were used as both counter and working electrodes, and silver wire was used as a reference at the beginning of the experiments by running cyclic voltammetry on ferrocene as the internal standard. Polymer thin films were formed by drop-casting 1.0 mm³ of polymer solutions in THF (1 mg/mL) on the working electrode and were then dried in air.



Scheme 1. Synthetic route to the random copolymers PThBTD_mCz_n.

2.3. Photovoltaic device fabrication and testing

Glass slides patterned with ITO (Colorado Concept Coatings LLC) were cleaned by sonicating sequentially in detergent, water, 1,1,1-trichloroethane, acetone and methanol, followed by treatment in a low power air plasma for 15 min with a Harrick PDC-32G plasma sterilizer. Thereafter, the ITO-coated slides were spin-coated (500 rpm for 5 s, then 4000 rpm for 60 s) with a filtered (0.45 μm NYL w/GMF syringe filter) aqueous solution of poly(ethylene dioxythiophene) doped with polystyrene sulphonic acid, PEDOT:PSS (Baytron P, H.C. Starck) and then transferred to a dry-box. The resulting thin PEDOT:PSS layer (~ 35 nm) was dried in an oven under a mild N_2 purge at 120 $^\circ\text{C}$ for 1 h. A chlorobenzene solution of polymer and PCBM (15.0 mg/mL each) was stirred at 50 $^\circ\text{C}$ for 16 h and then spun-cast on the PEDOT:PSS-coated slides for 90 s. The Al top electrode (~ 100 nm) was then deposited by thermal evaporation through a shadow mask to produce an active area of 0.12 cm^2 for each cell. The thickness of organic layer is determined by DEKTAK 6 M Stylus profiler. Preliminary testing of each of the 10 pixels was performed to select the most promising pixel prior to full solar simulated analysis. The best performing pixel then underwent V_{oc} , I_{sc} , dark and illuminated I - V studies using an Oriol 300 watt solar simulator with appropriate filters to provide AM 1.5G (100 mW/cm^2). The fill-factor (FF) was determined from the illuminated I - V and is the maximum power delivered divided by the product of V_{oc} and I_{sc} . The EQE was measured at a chopping frequency of 280 Hz with a lock-in amplifier (Stanford, SR830) during illumination with the mono-chromatic light from a Xenon lamp. Current-voltage (I - V) characteristics were recorded using a computer-controlled Keithley 236 source meter in the dark and under white light (CHF-XM 500 W Xenon lamp) illumination.

2.3.1. Monomer and polymer syntheses

The dibromonated monomer **1** was synthesized from commercially available 2,1,3-benzothiadiazole via a divergent method according to our recent publication [8]. 5,5'-Bis(trimethylstannyl)-2,2'-bithiophene [13] and *N*-octyl-2,7-dibromocarbazole [14] were prepared based on literature procedures.

2.3.2. General procedure for the preparation of random copolymers PThBTD_mCz_n

To a solution of dibrominated monomer **1** (0.3 mmol), monomer **3** (0.3 mmol) and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene **2** (0.6 mmol) in anhydrous chlorobenzene (5 mL), tetra(triphenylphosphine)palladium(0) (7 mg, 0.006 mmol) was added in glove box. The reaction mixture was stirred at ambient temperature for 5 min and then heated to reflux for 48 h under argon. 2-(Trimethylstannyl)thiophene (10 mg) was added, and 8 h later 2-bromothiophene (15 mg) was added and allowed to react for further 8 h. After the solution was cooled down to room temperature, the polymer was precipitated in methanol and collected by filtration. Dark solid obtained was first extracted with hexanes on Soxhlet extraction apparatus to remove low molecular weight oligomers, and then extracted

out with chlorobenzene. The chlorobenzene solution was concentrated under reduced pressure and re-precipitated in methanol. The purified polymer was collected and dried in vacuum oven at 80 $^\circ\text{C}$.

PThBTD₈Cz₂: 0.60 g, 69% yield. GPC: M_n : 10,400, M_w/M_n = 1.27 (relative to polystyrene standards). ^1H NMR (500 MHz, CDCl_3): δ (ppm) = 8.06 (br, 2H); 7.97 (br, 2H); 7.82 (br, 2H); 7.61 (br, 2H); 7.38 (br, 2H); 7.16 (br, 4H); 7.07 (br, 6H); 4.33 (br, 2H); 2.81 (br, 8H); 1.73 (br, 10H); 1.45–1.20 (br, 50H); 0.89 (br, 15H).

PThBTD₇Cz₃: 0.51 g, 62% yield. GPC: M_n : 9700, M_w/M_n = 1.13 (relative to polystyrene standards). ^1H NMR (500 MHz, CDCl_3): δ (ppm) = 8.06 (br, 2H); 7.98 (br, 2H); 7.80 (br, 2H); 7.67 (br, 2H); 7.38 (br, 2H); 7.16 (br, 4H); 7.06 (br, 6H); 4.35 (br, 2H); 2.88 (br, 8H); 1.74 (br, 10H); 1.45–1.25 (br, 50H); 0.89 (br, 15H).

PThBTD₅Cz₅: 0.50 g, 67% yield. GPC: M_n : 8600, M_w/M_n = 1.80 (relative to polystyrene standards). ^1H NMR (ODCB-*d*₄): δ (ppm) = 8.06 (br, 2H); 7.97 (br, 2H); 7.81 (br, 2H); 7.66 (br, 2H); 7.38 (br, 2H); 7.16 (br, 4H); 7.07 (br, 6H); 4.27 (br, 2H); 3.01 (br, 8H); 1.86 (br, 10H); 1.57–1.23 (br, 50H); 0.93 (br, 15H).

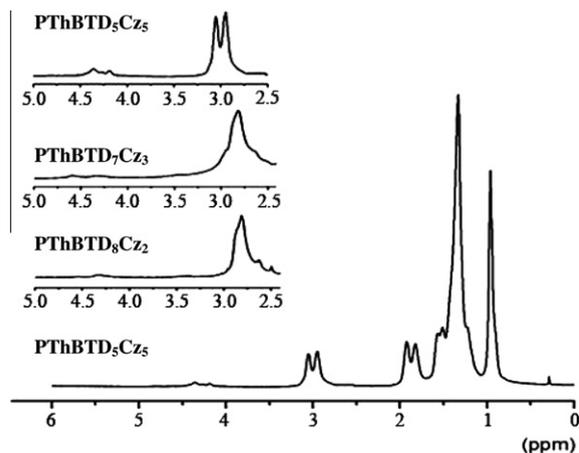
3. Results and discussion

3.1. Synthesis

The synthesis of the copolymers PThBTD_mCz_n is depicted in Scheme 1. The regioregular oligothiophene dibromides containing an electron-accepting benzothiadiazole core was prepared according to our previously reported procedure, which is very soluble in common organic solvents, allowing convenient purification by flash chromatography [8,12]. The other two monomers, 5,5'-bis(trimethylstannyl)-2,2'-bithiophene [13] and 2,7-dibromo-9-octyl-carbazole [14] were synthesized based on literature methods. The copolymers were synthesized by the Stille reaction of above three monomers in refluxing chlorobenzene using Pd(PPh₃)₄ as the catalyst under Ar. The composition of these random copolymers can be varied by adjusting the feed molar ratio between two monomers **M1** and **M3**. The resulting polymers (PThBTD₈Cz₂, PThBTD₇Cz₃ and PThBTD₅Cz₅) were purified by multiple dissolution/precipitation. All the copolymers were obtained as a deep-dark powder and can be easily dissolved in chlorinated solvents such as chloroform, chlorobenzene and dichlorobenzene. It was found that further increase the content of the carbazole unit within the polymer by changing the feed ratio of **M3** became impossible due to the poor solubility of the resulting polymer in common organic solvent. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) against polystyrene standard in THF eluent and the M_n were found to be in the range of 8600–11,000 with a narrow polydispersity index (M_w/M_n) of 1.13–1.80 (Table 1). The actual ratio of carbazole unit to benzothiadiazole unit in each polymer was estimated on the basis of the ^1H NMR spectra of the polymers (Fig. 1). In the ^1H NMR spectra of these polymers, there is a peak at δ 4.27–4.35 ppm which is attributed to the hydrogen of methylene attached directly on the nitrogen atom of carbazole moiety, while the

Table 1Fundamental physical data for random copolymers PThBTD_mCz_n.

Polymers	M_n^a	M_w^a	PDI ^a	T_g (°C)	T_d (°C)	T_m (°C)	T_c (°C)
PThBTD ₈ Cz ₂	10,400	13,200	1.27	109	439	190	162
PThBTD ₇ Cz ₃	9700	12,600	1.13	–	442	194	156
PThBTD ₅ Cz ₅	8600	15,400	1.80	115	420	–	–

^a Determined by GPC against polystyrene standards.**Fig. 1.** ¹H NMR of the copolymers PThBTD_mCz_n for the determination of the composition.

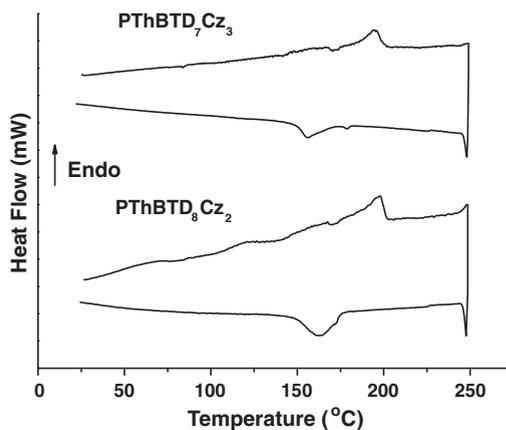
chemical shifts at 2.81–3.01 ppm were attributed to the hydrogen of methylene group at the 3-position of the thiynyls adjacent to the benzothiadiazole moiety. Therefore, the ratio of $m:n$ in these polymers could be determined by the ratio of the integral areas of these two peaks. The $m:n$ ratios determined in this way are 51:49 for PThBTD₅Cz₅, 72:28 for PThBTD₇Cz₃ and 81:19 for PThBTD₈Cz₂.

3.2. Thermal properties

The thermal property of the copolymers was investigated by DSC and TGA (Table 1). All the polymers have good thermal stability with 5% weight-loss temperature (T_d) higher than 410 °C under nitrogen. The crystallinity properties were investigated by DSC. All the polymers exhibited crystallization peaks in the DSC cooling curves, indicating these polymers are highly crystalline and have a strong tendency to crystallize. Specifically, the DSC curves of PThBTD₈Cz₂ and PThBTD₇Cz₃ at a heating–cooling rate of 10 °C min⁻¹ under nitrogen were given in Fig. 2. They showed crystallization peaks at 156 °C and 162 °C, respectively, and PThBTD₈Cz₂ exhibited a glass transition temperature at 109 °C.

3.3. Optical properties

The absorption spectra of PThBTD_mCz_n measured in chlorobenzene is characterized as two strong absorption bands at both shorter wavelength (~460–472 nm) corresponding to higher energy transitions such as π – π^* transition and longer wavelength at 619–630 nm, corresponding to the

**Fig. 2.** DSC curves of PThBTD₈Cz₂ and PThBTD₇Cz₃ at a heating–cooling rate of 10 °C min⁻¹ under nitrogen.

intramolecular charge-transfer (ICT) transition (Fig. 3). Weak absorption peaks located at ~700 nm were observed for all the polymers in the dilute solution, indicating the existence of the intermolecular aggregation among the polymer chains [15]. We also measured the absorption spectra of the polymer thin film spin-coated from dichlorobenzene solution using a slow solvent evaporation process. Compared with that in solution, the polymers showed pronounced red-shifted and broad absorption bands in thin film state (Fig. 3). No matter in solution or in film state, the variation of the relative content of the benzothiadiazole and carbazole segments within the polymers, the intensity of the two absorption bands will change accordingly. Generally, the increasement of the content of carbazole/benzothiadiazole moiety will enhance the high/low energy absorption intensity. For polymers PThBTD₈Cz₂ and PThBTD₇Cz₃, the intensity of two types of absorption is nearly equal in the film state. A distinct advantage in absorption property between these series of polymers and some carbazole/indolocarbazole-containing polymers reported by Leclerc and us previously, is that the absorption bands located at the higher and lower energy region are overlapped, leading to a quite broad absorption band ranging from 350 to 800 nm with the full width at half maximum of 334–367 nm (Table 2) [7,8]. It should be noted that such a broad absorption covering the whole visible region was originated from a single semiconducting polymer. In order to further evaluate the absorption property, polymer PThBTD₇Cz₃ was selected to compare its absorbance with known P3HT and the solar spectrum (Fig. 4). Clearly, PThBTD₇Cz₃ shows more satisfactory absorption than P3HT, and is more close to the solar spectrum. The excellent absorption property of

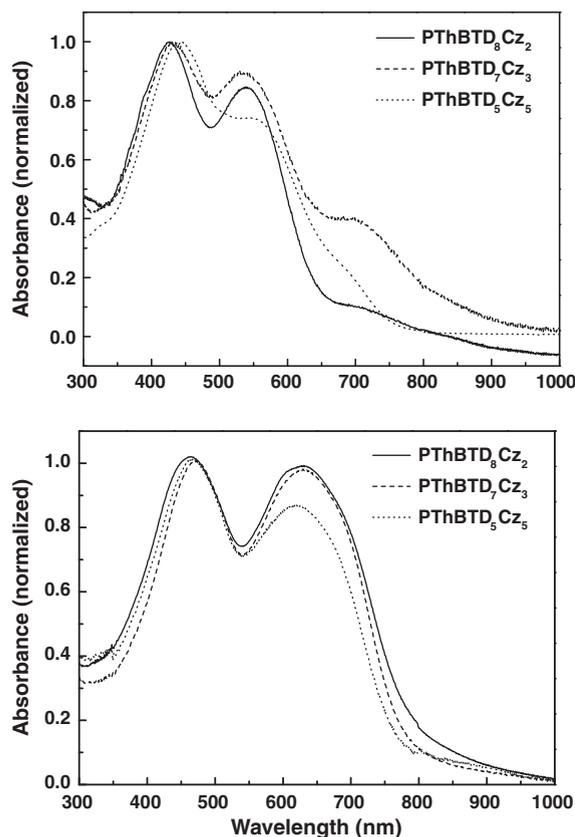


Fig. 3. UV-vis absorption spectra of PThBTD_mCz_n in chlorobenzene (top) and in film (bottom).

these polymers makes them ideal candidates as photovoltaic materials.

3.4. Electrochemical properties

To probe the electrochemical property of polymers, cyclic voltammetry (CV) measurements of copolymers PThBTD_mCz_n were carried out under argon in a three-electrode cell using 0.1 M Bu₄NClO₄ in anhydrous CH₃CN as the supporting electrolyte. The polymers were coated on the platinum-working electrode. The CV curves were recorded referenced to an Ag quasi-reference electrode, which was calibrated using a ferrocene/ferrocenium (Fc/Fc⁺) redox couple (4.8 eV below the vacuum level) as an external standard. The $E_{1/2}$ of the Fc/Fc⁺ redox couple was found to be

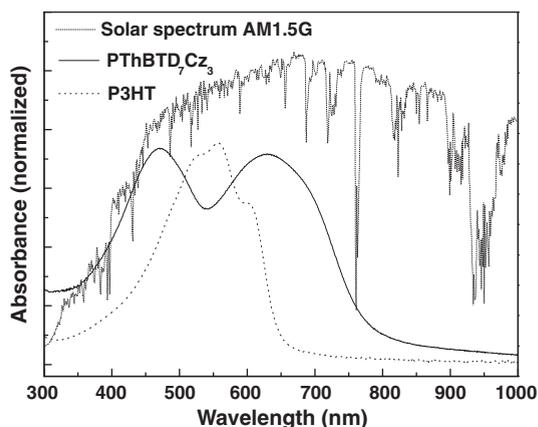


Fig. 4. UV-vis spectra of PThBTD₇Cz₃ in the solid state, P3HT as cast, and the solar spectrum.

0.40 V vs the Ag quasi-reference electrode. Therefore, the HOMO and LUMO energy levels of the copolymers can be estimated using the empirical equation $E_{\text{HOMO}} = -(E_{\text{ox}}^{\text{on}} + 4.40)$ eV and $E_{\text{LUMO}} = -(E_{\text{red}}^{\text{on}} + 4.40)$ eV, respectively, where $E_{\text{ox}}^{\text{on}}$ and $E_{\text{red}}^{\text{on}}$ stand for the onset potentials for oxidation and reduction relative to the Ag quasi-reference electrode, respectively [16]. The cyclic voltammograms of the polymers are shown in Fig. 5. Upon cathodic scan, three couples of reversible reduction peaks were observed, corresponding to the redox process of benzothiadiazole, thiophene and carbazole units, respectively [17]. In the anodic scan, two couples of oxidation peaks were observed, corresponding to the redox process of carbazole and thiophene units, respectively [18,19]. The good cyclic voltammetry properties exhibited by the three polymers indicates these materials are beneficial for both hole and electron injection. However, it is interesting to point out that the current density of *p*-doping process was much bigger than that of *n*-doping process. As can be seen from Table 2, the incorporation of electron-withdrawing benzothiadiazole units into the polymer backbone led to narrower energy gaps, in comparison with P3HT. Meanwhile, the HOMO energy levels of the three polymers remain low at ~ 5.10 eV, which are important for achieving the large open-circuit voltage (V_{oc}) and high air stability. Deep-HOMO conjugated polymers have been particularly emphasized to achieve the maximum potential in recent literature [20]. The electrochemical band gaps (E_{g}^{ec}) are larger than those of the optical band gaps ($E_{\text{g}}^{\text{opt}}$) for all three polymers. This difference can be explained by the exciton binding energy of conjugated polymers which is typically in the range of ~ 0.4 – 1.0 eV [21].

Table 2

Absorption and electrochemical properties of the random copolymers PThBTD_mCz_n.

Polymers	Absorption (nm) ^a			$E_{\text{g}}^{\text{opt}}$ (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{g}^{ec} (eV) ^c
	Short wavelength	Long wavelength	FWHM ^b				
PThBTD ₈ Cz ₂	463	630	367	1.59	−5.12	−3.34	1.78
PThBTD ₇ Cz ₃	470	631	343	1.62	−5.12	−3.33	1.79
PThBTD ₅ Cz ₅	465	619	341	1.64	−5.10	−3.32	1.78

^a Measured in film state.

^b Full width at half maximum.

^c Energy gap = HOMO–LUMO.

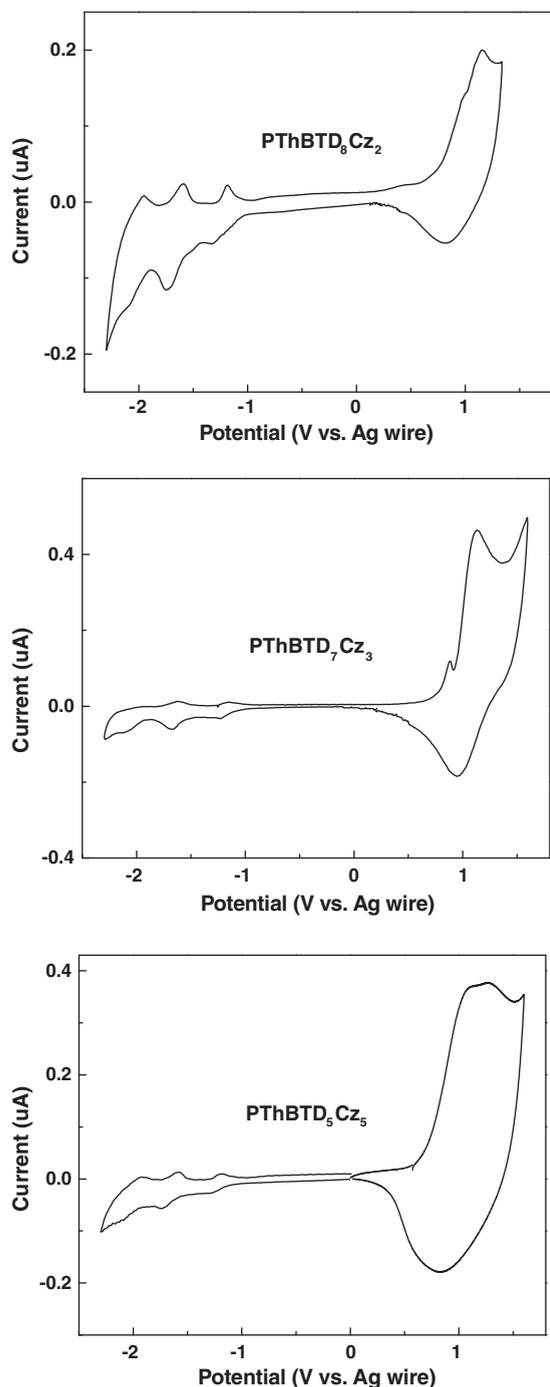


Fig. 5. CV curve of PThBTD_mCz_n film with 0.1 M Bu₄NClO₄ in acetonitrile as the supporting electrolyte at 100 mV s⁻¹.

3.5. Photovoltaic properties

The potential of these polymers used as a hole-transporting light-absorbing component in photovoltaic cells were explored. Bulk heterojunction PV cells with a device structure of ITO/PEDOT:PSS/PThBTD_mCz_n:PC₆₁BM (1:1, w/w)/LiF(1 nm)/Al(100 nm) were fabricated. The active layer

was spin-coated from dichlorobenzene solution using a slow solvent evaporation process [22]. The solar cells were fabricated with variable polymer: PCBM weight ratio, i.e., the w/w of polymer: PCBM is 1:*x* (*x* = 3, 2, 1). Fig. 6 shows the current density–voltage characteristics of polymer-PThBTD₅Cz₅ based devices with different PCBM loading under AM 1.5 simulated solar illumination of 100 mW/cm². It was observed that the increase of the amount of PCBM leads to the decrease of the short circuit current density (Table 3), while the open-circuit voltage gives no significant change. Finally, the PThBTD₅Cz₅:PCBM (1:1) device gave power conversion efficiency of 1.09% with $V_{oc} = 0.68$ V, short circuit current (J_{sc}) = 4.43 mA/cm², and fill-factor (FF) = 0.36. The low FF and short circuit indicate that the bulk heterojunctions suffer seriously from recombination loss and large serial resistance.

In the following work, we measured the external quantum efficiency (EQE) spectra for devices using PThBTD₅Cz₅:PCBM (w/w = 1:1, 1:2 and 1:3) blend as the photoactive layer, as depicted in Fig. 7. To our surprise, although the EQE profiles are broader about 100 nm than that of P3HT, which has no photoresponse above 650 nm, they are quite inconsistent with the absorption spectrum of PThBTD₅Cz₅ in film state, in view that there is almost no photoresponse in the low-energy band from 700 to 800 nm. One probable explanation for this phenomenon is that a large portion of the absorption between 700 and 800 nm was arisen from the intermolecular stacking, which may have no contribution to the photoresponse, as evidenced by the blue-shifted absorption spectrum of PThBTD₅Cz₅:PCBM (w/w = 1:1) blend, compared with that of PThBTD₅Cz₅ film (Fig. 7) [23]. In addition, it was also observed that the EQE spectra were strongly dependent on the amount of PCBM loading (Fig. 7), indicating that the charge-carrier separation may occur mainly at either separate conjugated segments of the random copolymer or both.

As for the other two polymers, PThBTD₇Cz₃ and PThBTD₈Cz₂, we need to increase the amount of PCBM to obtain a good PCE efficiency. This is consistent with the fact that the content of the electron-accepting benzothiadiazole is increasing and the content of carbazole units is

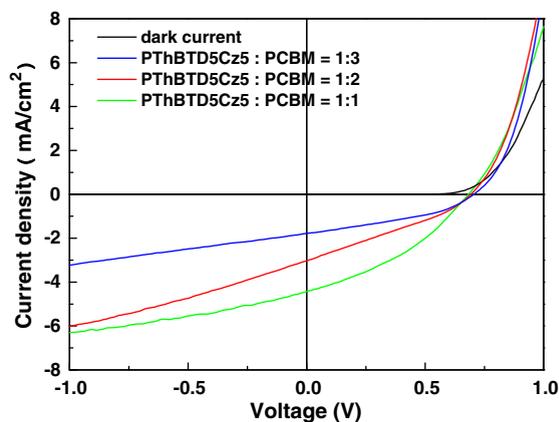
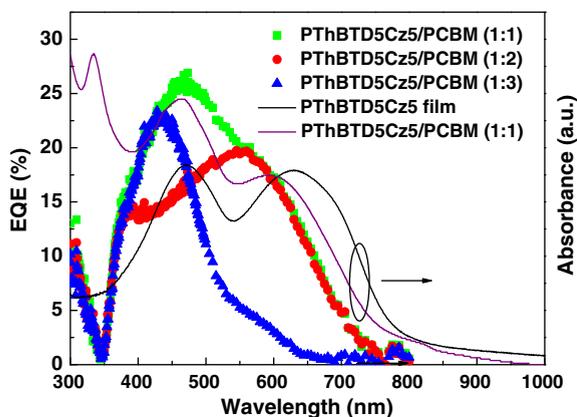


Fig. 6. Current density–voltage characteristics of polymer-PThBTD₅Cz₅ based devices with different PCBM loading (w/w = 1:3 1:2; and 1:1) under AM 1.5 simulated solar illumination of 100 mW/cm².

Table 3Photovoltaic properties of polymer solar cells.^{a,b}

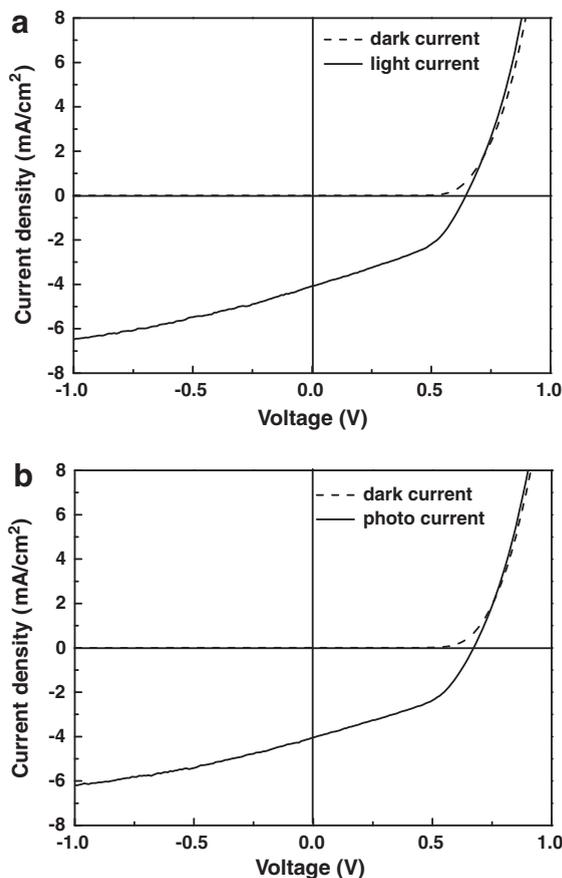
Polymers	Polymer:PCBM (wt/wt)	Thickness (nm)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	PCE (%)
PThBTD ₅ Cz ₅	1:3	180	0.70	1.78	0.38	0.47
PThBTD ₅ Cz ₅	1:2	120	0.69	3.02	0.30	0.62
PThBTD ₅ Cz ₅	1:1	110	0.68	4.43	0.36	1.09
PThBTD ₇ Cz ₃	1:2	75	0.64	3.23	0.47	1.12
PThBTD ₈ Cz ₂	1:2	70	0.67	4.04	0.44	1.18

^a Under simulated AM 1.5 solar illumination at an irradiation intensity of 100 mW/cm².^b For as-fabricated devices.**Fig. 7.** External quantum efficiency spectra of PThBTD₅Cz₅/PCBM based PV devices. The absorption spectra of PThBTD₅Cz₅ film and PThBTD₅Cz₅/PCBM (1:1) blend were also shown.

decreasing, compared with that of PThBTD₅Cz₅. As a result, the solar cells based on these two polymers gave similar PCE of 1.1–1.2% with V_{oc} of 0.64–0.68 V when blended with PCBM in the weight ratio of 1:2. Fig. 8 shows the corresponding current–voltage characteristics of the fabricated PV cells in the dark and under the AM 1.5 simulated solar illumination at irradiation intensity of 100 mW/cm². The device performance was summarized in Table 3. It should be noted that, contrary to P3HT based solar cells, thermal annealing did not improve the device performance, although polymer crystallization was observed in the DSC measurement. Such a phenomenon has been found in our recent study on the photovoltaic properties of newly synthesized highly crystallized alternating hexa-/octathiophenes–benzothiadiazole copolymers [24].

4. Conclusions

Low-bandgap conjugated polymers containing content-tunable hole-transporting carbazole units and electron-accepting 2,1,3-benzothiadiazole moieties have been synthesized. The broad absorption covering from 300 to 800 nm range was realized by fine selection of appropriate building blocks, based on that different conjugation segments corresponds to different wavelength absorption, along with the absorption from strong interchain stacking. The concept demonstrates an efficient and new way to realize full absorption through a single polymer. The transport ability can also be adjusted by varying the composition in random copolymers. The preliminary investigation

**Fig. 8.** Current density–voltage characteristics of polymer (a) PThBTD₇Cz₃, and (b) PThBTD₈Cz₂ based devices under AM 1.5 simulated solar illumination of 100 mW/cm².

on the photovoltaic device of the PThBTD_mCz_n polymers gave similar power conversion efficiency of 1.1–1.2% with V_{oc} of 0.64–0.68 V under simulated solar light AM 1.5 G (100 mW/cm²). Further work on the optimization of the solar cell devices and fabrication of tandem solar cells using the synthesized polymers and P3HT as the photoactive materials is ongoing.

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